

Synthesis of some bischromophoric dyes containing nonabsorbing flexible bridge

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Bis-chromophoric dyes (9-68) having nonabsorbing flexible bridges have been synthesised by the condensation of 1,1'-alkylenebis (α/γ picolinium bromides) (1-8) with aromatic aldehydes.

Zimmerman *et al.*¹⁻⁴ have synthesised some compounds with aromatic chromophores containing a spacer which have the capacity to trap organic molecules of different sizes and called these compounds as "Molecular tweezers". These molecular tweezers with an interchromophoric distance of about 7 Å can form complex with guest molecules of unrestricted length and width provided they have the thickness of a single aromatic ring. We have made an attempt to synthesise a series of such compounds with styryl chromophores having nonabsorbing flexible chains as spacer.

The reaction sequence leading to the formation of the styryl dyes is outlined in Scheme 1. Alkylation of α - and γ -picolines was carried out with

dibromoalkanes of different chain lengths. Among the 1,1'-alkylenebis (picolinium bromides), 1 and 5 were isolated as semisolids (probably due to low melting point and hygroscopic character) and the rest as crystalline solids (cf. Table 1). These compounds were further condensed with aromatic aldehydes and cinnamaldehyde to yield the intense coloured dyes (9-68; Table 2). The styryl dyes, thus prepared, showed characteristics absorption maxima in water in the range 370-470 nm at $10^{-5}M$ concentration. However, with the change in dye concentration the

Table 1—Melting points and yields of 1,1'-alkylenebis (picolinium bromides) (1-8)

| Compound | n | Picoline used | m.p. °C | Yield (%) |
|----------|---|---------------|---------|-----------|
| 1 | 2 | γ | * | — |
| 2 | 3 | γ | 64-65 | 95 |
| 3 | 4 | γ | 73-74 | 95 |
| 4 | 6 | γ | 65-66 | 90 |
| 5 | 2 | α | * | — |
| 6 | 3 | α | 66-67 | 95 |
| 7 | 4 | α | 75-76 | 90 |
| 8 | 6 | α | 69-70 | 90 |

* Hygroscopic

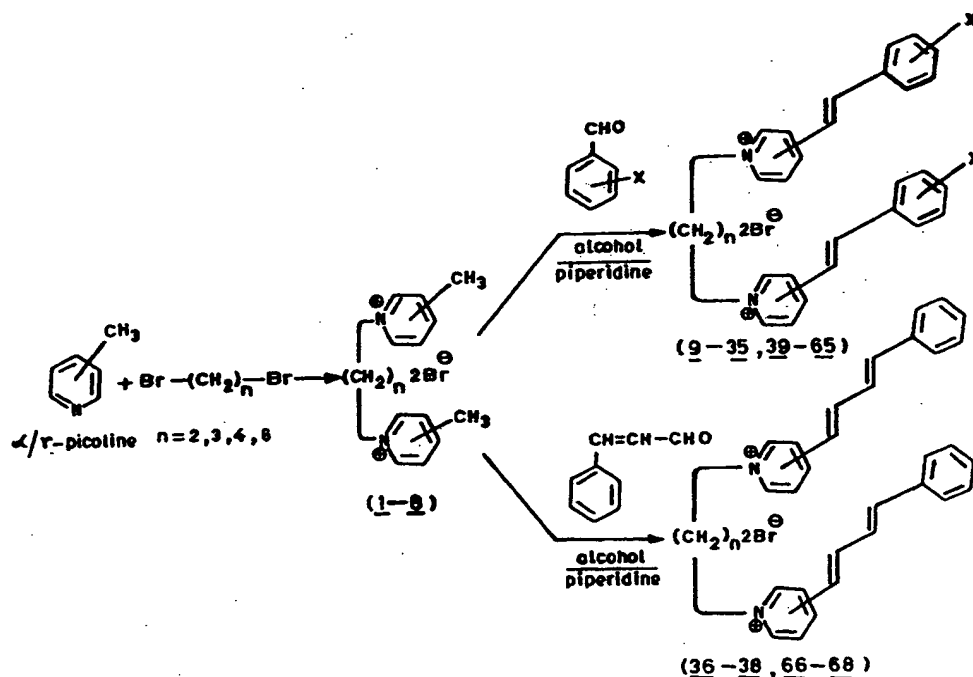


Table 2—Characterisation data of the styrylpyridinium dyes (9-68)

| Compd | n | Position of styryl group | X | Yield (%) | m.p. °C | UV (Water) nm (log ε) | Found (%) (Calc.) | | |
|-------|---|-----------------------------|----------------------------|--------------|------------|-----------------------------|-------------------|------------|--------------|
| | | | | | | | C | H | Br |
| 9 | 2 | 4 | <i>p</i> -OCH ₃ | 43 | 266 | 386 (4.6836) | 59.1 (59.0) | 4.8 4.9 | 25.9 26.2 |
| 10 | 3 | 4 | <i>p</i> -OCH ₃ | 46 | 264 | 380 (4.7538) | 59.7 (59.6) | 5.0 5.1 | 25.4 25.6 |
| 11 | 4 | 4 | <i>p</i> -OCH ₃ | 58 | 267 | 376 (4.5897) | 60.0 (60.2) | 5.3 5.3 | 24.9 25.0 |
| 12 | 6 | 4 | <i>p</i> -OCH ₃ | 60 | 260 | 371 (4.3176) | 61.2 (61.3) | 5.6 5.7 | 23.7 24.0 |
| 13 | 2 | 4 | <i>p</i> -NMe ₂ | 32 | 276 | 474 (4.7229) | 60.2 (60.4) | 5.8 5.7 | 24.9 25.2 |
| 14 | 3 | 4 | <i>p</i> -NMe ₂ | 65 | 290 | 470 (4.7310) | 61.0 (60.9) | 5.7 5.8 | 24.5 24.6 |
| 15 | 4 | 4 | <i>p</i> -NMe ₂ | 70 | 291 | 463 (4.7481) | 61.5 (61.4) | 5.9 6.0 | 23.6 24.1 |
| 16 | 6 | 4 | <i>p</i> -NMe ₂ | 70 | 255 | 458 (4.7167) | 62.2 (62.4) | 6.1 6.4 | 22.9 23.1 |
| 17 | 2 | 4 | <i>o</i> -OH | 30 | 237 | 390 (4.6639) | 57.8 (57.7) | 4.5 4.5 | 27.1 27.5 |
| 18 | 3 | 4 | <i>o</i> -OH | 50 | 240 | 382 (4.7149) | 58.4 (58.4) | 4.5 4.7 | 26.4 26.8 |
| 19 | 4 | 4 | <i>o</i> -OH | 68 | 271 | 376 (4.5673) | 58.9 (59.0) | 4.9 4.9 | 25.8 26.2 |
| 20 | 6 | 4 | <i>o</i> -OH | 72 | 280 | 370 (4.4235) | 60.4 (60.2) | 5.1 5.3 | 24.8 25.1 |
| 21 | 3 | 4 | <i>p</i> -Cl | 30 | 97 | 357 (4.2489) | 54.8 (55.0) | 4.1 4.1 | 25.0 25.3 |
| 22 | 4 | 4 | <i>p</i> -Cl | 34 | 98 | 368 (4.3155) | 55.5 (55.6) | 4.2 4.3 | 24.5 24.7 |
| 23 | 6 | 4 | <i>p</i> -Cl | 38 | 96 | 395 (4.2964) | 51.8 (51.7) | 5.2 5.3 | 26.2 26.5 |
| 24 | 3 | 4 | <i>m</i> -NO ₂ | 66 | 262 | 348 (4.3146) | 53.2 (53.2) | 3.8 4.0 | 24.1 24.5 |
| 25 | 4 | 4 | <i>m</i> -NO ₂ | 70 | 269 | 342 (4.2854) | 53.6 (53.9) | 4.2 4.2 | 23.7 24.0 |
| 26 | 6 | 4 | <i>m</i> -NO ₂ | 68 | 273 | 339 (4.2247) | 55.2 (55.3) | 4.2 4.3 | 22.7 23.1 |
| 27 | 3 | 4 | <i>p</i> -NO ₂ | 70 | 290 | 330 (4.3877) | 52.9 (53.2) | 4.0 4.0 | 23.9 24.5 |
| 28 | 4 | 4 | <i>p</i> -NO ₂ | 74 | 272 | 322 (4.3447) | 53.9 (53.9) | 4.2 4.2 | 23.5 24.0 |
| 29 | 6 | 4 | <i>p</i> -NO ₂ | 68 | 274 | 318 (4.2193) | 55.4 (55.3) | 4.1 4.3 | 22.8 23.1 |
| 30 | 3 | 4 | H | 68 | 290 | 375 (4.2363) | 61.6 (61.7) | 5.1 5.0 | 28.0 28.4 |
| 31 | 4 | 4 | H | 73 | 270 | 385 (4.1986) | 62.2 (62.3) | 5.0 5.2 | 27.4 27.7 |
| 32 | 6 | 4 | H | 74 | 268 | 389 (4.1658) | 63.1 (63.4) | 5.6 5.6 | 26.0 26.4 |
| 33 | 3 | 4 | <i>o</i> -Cl | 60 | 290 | 346 (4.2012) | 55.1 (55.0) | 3.9 4.1 | 25.1 25.3 |
| 34 | 4 | 4 | <i>o</i> -Cl | 65 | 266 | 340 (4.2332) | 55.6 (55.6) | 4.4 4.3 | 24.2 24.7 |

(Contd.)

Table 2—Characterisation data of the styrylpyridinium dyes (9-68)—Contd

| Compd | n | Position of styryl group | X | Yield (%) | m.p. °C | UV (Water) nm (log ε) | Found (%) (Calc.) | | |
|-------|---|--------------------------|----------------------------|-----------|---------|-----------------------|-------------------|------------|--------------|
| | | | | | | | C | H | Br |
| 35 | 6 | 4 | <i>o</i> -Cl | 69 | 273 | 338 (4.1976) | 51.4 (51.7) | 5.4 5.3 | 26.4 26.5 |
| 36 | 3 | 4 | — | 70 | 268 | 420 (4.3122) | 69.9 (70.3) | 5.5 5.2 | 20.7 20.8 |
| 37 | 4 | 4 | — | 73 | 279 | 416 (4.2878) | 64.7 (64.8) | 5.3 5.4 | 24.9 25.4 |
| 38 | 6 | 4 | — | 77 | 280 | 411 (4.2645) | 71.3 (71.1) | 5.5 5.7 | 19.1 19.8 |
| 39 | 2 | 2 | <i>p</i> -OCH ₃ | 55 | 268 | 370 (4.5944) | 59.3 (59.0) | 4.7 4.9 | 25.8 26.2 |
| 40 | 3 | 2 | <i>p</i> -OCH ₃ | 60 | 270 | 374 (4.6163) | 59.4 (59.6) | 5.2 5.1 | 25.0 25.6 |
| 41 | 4 | 2 | <i>p</i> -OCH ₃ | 64 | 270 | 382 (4.5543) | 60.4 (60.2) | 5.4 5.3 | 24.9 25.0 |
| 42 | 6 | 2 | <i>p</i> -OCH ₃ | 62 | 271 | 390 (4.4880) | 61.1 (61.3) | 5.8 5.7 | 23.9 24.0 |
| 43 | 2 | 2 | <i>p</i> -NMe ₂ | 70 | 274 | 380 (4.6845) | 60.5 (60.4) | 5.5 5.7 | 24.7 25.2 |
| 44 | 3 | 2 | <i>p</i> -NMe ₂ | 66 | 282 | 386 (4.6967) | 61.2 (60.9) | 5.7 5.8 | 24.1 24.6 |
| 45 | 4 | 2 | <i>p</i> -NMe ₂ | 63 | 280 | 444 (4.6300) | 58.9 (59.0) | 5.0 4.9 | 25.8 26.2 |
| 46 | 6 | 2 | <i>p</i> -NMe ₂ | 74 | 258 | 470 (4.3860) | 62.2 (62.4) | 5.9 6.4 | 22.7 23.1 |
| 47 | 2 | 2 | <i>o</i> -OH | 32 | 238 | 352 (4.5870) | 57.8 (57.7) | 4.2 4.5 | 27.0 27.5 |
| 48 | 3 | 2 | <i>o</i> -OH | 68 | 220 | 358 (4.6339) | 58.1 (58.4) | 4.6 4.7 | 26.2 26.8 |
| 49 | 4 | 2 | <i>o</i> -OH | 75 | 210 | 374 (4.6145) | 53.9 (53.9) | 4.0 4.2 | 23.7 23.9 |
| 50 | 6 | 2 | <i>o</i> -OH | 71 | 235 | 392 (4.3170) | 60.0 (60.2) | 5.5 5.3 | 24.7 25.1 |
| 51 | 3 | 2 | <i>p</i> -Cl | 55 | 270 | 376 (4.3243) | 55.2 (55.0) | 3.9 4.1 | 25.0 25.3 |
| 52 | 4 | 2 | <i>p</i> -Cl | 64 | 285 | 381 (4.3176) | 55.5 (55.6) | 4.0 4.3 | 24.1 24.7 |
| 53 | 6 | 2 | <i>p</i> -Cl | 67 | 250 | 387 (4.2489) | 51.5 (51.7) | 5.2 5.3 | 26.4 26.5 |
| 54 | 3 | 2 | <i>m</i> -NO ₂ | 70 | 269 | 340 (4.3122) | 53.0 (53.2) | 4.1 4.0 | 24.0 24.5 |
| 55 | 4 | 2 | <i>m</i> -NO ₂ | 73 | 273 | 342 (4.2850) | 53.7 (53.9) | 4.2 4.2 | 23.6 24.0 |
| 56 | 6 | 2 | <i>m</i> -NO ₂ | 74 | 278 | 351 (4.2027) | 55.5 (55.3) | 4.0 4.3 | 22.8 23.1 |
| 57 | 3 | 2 | <i>p</i> -NO ₂ | 72 | 273 | 340 (4.3860) | 53.0 (53.2) | 4.1 4.0 | 24.0 24.5 |
| 58 | 4 | 2 | <i>p</i> -NO ₂ | 76 | 265 | 376 (4.3500) | 54.0 (53.9) | 4.0 4.2 | 23.8 24.0 |
| 59 | 6 | 2 | <i>p</i> -NO ₂ | 78 | 269 | 384 (4.2435) | 55.0 (55.3) | 4.4 4.3 | 22.6 23.1 |
| 60 | 3 | 2 | H | 77 | 245 | 380 (4.4633) | 61.6 (61.7) | 4.8 5.0 | 27.8 28.4 |

(Contd.)

Table 2—Characterisation data of the styrylpyridinium dyes (9-68) —Contd

| Compd | n | Position of styryl group | X | Yield (%) | m.p. °C | UV (Water) nm (log ϵ) | Found (%) (Calc.) | | |
|-------|---|--------------------------|--------------|-----------|---------|---------------------------------|-------------------|-----------|-------------|
| | | | | | | | C | H | Br |
| 61 | 4 | 2 | H | 72 | 282 | 382 (4.3875) | 62.1 (62.3) | 5.1 (5.2) | 27.4 (27.7) |
| 62 | 6 | 2 | H | 69 | 279 | 386 (4.1154) | 63.0 (63.4) | 5.7 (5.6) | 26.2 (26.4) |
| 63 | 3 | 2 | <i>o</i> -Cl | 65 | 283 | 364 (4.4597) | 55.1 (55.0) | 4.0 (4.1) | 24.7 (25.3) |
| 64 | 4 | 2 | <i>o</i> -Cl | 69 | 262 | 367 (4.3877) | 55.6 (55.6) | 4.3 (4.3) | 24.7 (24.7) |
| 65 | 6 | 2 | <i>o</i> -Cl | 61 | 265 | 371 (4.3110) | 51.5 (51.7) | 5.4 (5.3) | 25.9 (26.5) |
| 66 | 3 | 2 | — | 73 | 258 | 410 (4.2870) | 70.2 (70.3) | 5.1 (5.2) | 20.3 (20.8) |
| 67 | 4 | 2 | — | 54 | 260 | 416 (4.2956) | 64.9 (64.8) | 5.3 (5.4) | 25.2 (25.4) |
| 68 | 6 | 2 | — | 68 | 271 | 421 (4.1875) | 70.9 (71.1) | 5.7 (5.7) | 19.1 (19.8) |

spectra showed anomalous behaviour due to aggregation of the dyes.

Interestingly enough the 4-styryl dyes having electron donating groups suffered a bathochromic shift on decreasing the chain length of the bridge whereas those with electron withdrawing groups and 2-styryl dyes underwent a hypsochromic shift. The bathochromic shift in the former may be attributed to the inductive effect of styrylpyridinium alkyl derivative on the other styrylpyridinium part. Charton⁵ has tabulated the inductive parameters of a series of bromoalkyl groups (σ values of Br-CH₂- = 0.20; Br-CH₂-CH₂- = 0.05 and Br-CH₂-CH₂-CH₂- = 0.02 and the corresponding pK_a values of 4-substituted bicyclo[2, 2, 2]octane-1-carboxylic acids are 3.99, 4.58 and 4.72 respectively) and showed that with increasing chain length the inductive effect decreases. Substituent at = N⁺ of pyridinium group with high inductive values will enhance the electron flow from the auxochrome to the quaternary nitrogen. But in the case of 2-styryl dyes the steric effect predominates. With increasing methylene chain the steric effect decreases due to "distant effect" of heavy group from the chromophore. Heddon and Brown⁶ have also reported a hypsochromic shift of 4-5 nm in benzocyclalkanone on increasing the methylene chain (from 4 to 5 methylene groups) bridged at *ortho*-positions.

The characteristic IR bands appeared at 3000 (aromatic C-H), 1600 (CS=N) and 1550 cm⁻¹ (C=C). The PMR spectra of these compounds suggested that the styryl derivatives are *trans* in all

cases. A doublet at δ 7.45 with a coupling constant of 16 Hz for the ethenic protons supported the *trans*-configuration of the dyes. Other characteristic signals appeared at δ 1.70 (t, terminal -CH₃), 3.95 (s, -OCH₃), 4.70 (q, = N⁺-CH₂-) and 8.00-9.00 (aromatic protons, d for *para* derivatives and complex for *ortho* or *meta* derivatives). The protons of β -methylene groups appeared at δ 2.80 (complex) and those of γ -methylene groups at 1.50 (complex). However, no significant change in spectral data due to variance in chain length of the bridge was observed.

Experimental

Melting point were taken on a Yorco melting point apparatus and are uncorrected. UV and IR spectra were recorded on Hitachi-200 and Perkin Elmer-398 spectrophotometers, respectively, and PMR spectra on an EM-360 instrument in CDRI, Lucknow.

1,1'-Ethylenebis (γ -picolinium bromide) (1)

A mixture of γ -picoline (1.86 ml, 0.02 mole) and 1,2-dibromoethane (0.94 ml, 0.01 mole) was refluxed on a water-bath for 6 hr. The semisolid, thus obtained, was washed with ether to give 1 (hygroscopic).

Using a similar procedure the 1,1'-alkylenebis (picolinium bromides) 2, 5 and 6 (Table 1) were synthesised.

1,1'-Butylenebis (γ -picolinium bromide) (3)

A mixture of γ -picoline (1.86 ml, 0.02 mole) and

1,4-dibromobutane (1.08 ml, 0.01 mole) was heated in a sealed tube in an oil-bath at 110°C for 6 hr. The solid mass, thus obtained, was washed with ether to give 3.

A similar procedure was adopted to prepare 4, 7 and 8 (Table 1).

1,1'-Ethylenebis γ -(4-methoxystyryl) pyridinium bromide (9)

An ethanolic solution (20 ml) of 1 (0.374 g, 0.001 mole) and anisaldehyde (0.27 ml, 0.002 mole) with two drops of piperidine was refluxed for 4 hr. The volume of the solution was reduced to a pasty mass which was washed with ether-acetone (4:1, v/v) and crystallised from 5% aq. ethanol to give 9.

The dyes, 10-68, were prepared by the above

procedure and their characterization data are given in Table 2.

Acknowledgement

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